

## PATENT COOPERATION TREATY

PCT


NOTIFICATION CONCERNING  
SUBMISSION OR TRANSMITTAL  
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

From the INTERNATIONAL BUREAU

To:

ISENBRUCK, Günter  
Isenbruck Bösl Hörschler Wichmann  
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Germany

B 1	
B 2	
B 3	
Sekr	
EDV	
Ablg	

Date of mailing (day/month/year) 23 September 2004 (23.09.2004)	<b>IMPORTANT NOTIFICATION</b>  International filing date (day/month/year) 29 July 2004 (29.07.2004)  Priority date (day/month/year) 31 July 2003 (31.07.2003)
Applicant's or agent's file reference B03-0567PC	
International application No. PCT/EP2004/008497	
International publication date (day/month/year) Not yet published	
Applicant BASF AKTIENGESELLSCHAFT et al	

- By means of this Form, which replaces any previously issued notification concerning submission or transmittal of priority documents, the applicant is hereby notified of the date of receipt by the International Bureau of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to a date of receipt, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
- (If applicable) The letters "NR" appearing in the right-hand column denote a **priority document which, on the date of mailing of this Form, had not yet been received by the International Bureau** under Rule 17.1(a) or (b). Where, under Rule 17.1(a), the priority document must be submitted by the applicant to the receiving Office or the International Bureau, but the applicant fails to submit the priority document within the applicable time limit under that Rule, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
- (If applicable) An asterisk(\*) appearing next to a date of receipt, in the right-hand column, denotes a **priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b)** (the priority document was received after the time limit prescribed in Rule 17.1(a) or the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b)). Even though the priority document was not furnished in compliance with Rule 17.1(a) or (b), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as priority document, Rule 17.1(c) provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
31 July 2003 (31.07.2003)	03016649.0	EP	10 Sept 2004 (10.09.2004)

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland  Facsimile No. (41-22) 338.70.80	Authorized officer  Christian TREICHEL  Telephone No. (41-22) 338 9237
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# PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

ISENBRUCK, Günter, Isenbruck | Bösl | Hörschler |  
Wichmann | Huhn, Patentanwälte  
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ALLEMAGNE

25. Juli 2005

Frist: 25. 8. 05  
Vorfrist:  
WV: not. coe

*M. Schall*  
**PCT**

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL PRELIMINARY  
REPORT ON PATENTABILITY  
(PCT Rule 71.1)

B 1	B
B 2	XS
B 3	
Sekr	
EDV	
Abtg.	

Date of mailing  
(day/month/year) 22.07.2005

Applicant's or agent's file reference B03-0567PC		<b>IMPORTANT NOTIFICATION</b>	
International application No. PCT/EP2004/008497	International filing date (day/month/year) 29.07.2004	Priority date (day/month/year) 31.07.2003	
Applicant BASF AKTIENGESELLSCHAFT et al.			


- The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary report on patentability and its annexes, if any, established on the international application.
- A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
- Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
- REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Brell, S Tel. +49 89 2399-7271
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# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference B03-0567PC		<b>FOR FURTHER ACTION</b>		See Form PCT/IPEA/416
International application No. PCT/EP2004/008497		International filing date (day/month/year) 29.07.2004		Priority date (day/month/year) 31.07.2003
International Patent Classification (IPC) or national classification and IPC C07F9/50				
Applicant BASF AKTIENGESELLSCHAFT et al.				
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 7 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau) a total of 3 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>				
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>				
Date of submission of the demand  20.04.2005		Date of completion of this report  22.07.2005		
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized Officer  Richter, H  Telephone No. +49 89 2399-8539		



**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/EP2004/008497

**Box No. I Basis of the report**

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
  - ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
    - ☐ international search (under Rules 12.3 and 23.1(b))
    - ☐ publication of the international application (under Rule 12.4)
    - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements\*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

**Description, Pages**

1-11 as originally filed

**Claims, Numbers**

1-9 received on 20.04.2005 with letter of 20.04.2005

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
  - ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
  - ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):

\* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/EP2004/008497

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**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

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1. Statement

Novelty (N)	Yes: Claims	1-9
	No: Claims	
Inventive step (IS)	Yes: Claims	
	No: Claims	1-9
Industrial applicability (IA)	Yes: Claims	1-9
	No: Claims	

2. Citations and explanations (Rule 70.7):

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
REPORT ON PATENTABILITY  
(SEPARATE SHEET)**

International application No.

PCT/EP2004/008497

**IAP20 Rec'd PCT/PTO 23 JAN 2006**

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

Reference is made to the following documents:

D1 = WO-A-00/32612

D2 = US-A- 5321148

D3 = US-A-5276219

D4 = US-A-5912378

D5 = GB-A-2280671

The document D1 is regarded as being the closest prior art to the subject-matter of claim and discloses (the references in parentheses applying to this document):

A process for the preparation of acyl phosphines of formula I (claim 1), wherein n is 1 (claims 5, 10)

R1 is

C1-C18-alkyl, C2-C18-alkyl which is interrupted by one or several non-successive O atoms; phenyl-substituted C1-C4-alkyl, C2-C8-alkenyl, phenyl, naphthyl, biphenyl, C5-C12-cycloalkyl or a 5-or 6-membered O-, S-or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl, C5-C12-cycloalkyl or the 5-or 6-membered O-, S-or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen, C1-C8-alkyl, C1-C8-alkylthio and/or C1-C8-alkoxy;

R2 is C1-C18-alkyl, C3-C12-cycloalkyl, C2-C8-alkenyl, phenyl, naphthyl, biphenyl or a 5-or 6 membered O-, S-or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl or 5-or 6-membered O-, S-or N-containing heterocyclic ring being unsubstituted or substituted by one to four C1-C8-alkyl, C1-C8-alkoxy, C1-C8-alkylthio and/or halogen;

R3 is C1-C18-alkyl, C2-C18-alkyl which is interrupted by one or several non-successive O atoms; phenyl-substituted C1-C4-alkyl, C2-C8-alkenyl, phenyl, naphthyl, biphenyl, C5-C12-cycloalkyl or a 5-or 6-membered O-, S-or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl, C5-C12-cycloalkyl or the 5-or 6-membered O-, S-or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen,

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C1-C8-alkyl,  
C1-C8-alkylthio and/or C1-C8-alkoxy;  
by (1) reacting organic phosphorus halides of formula (II)  
wherein R1, R3, and m have the meaning cited above,  
and Y is Br or Cl,  
with an alkali metal or with magnesium in combination with lithium, or with mixtures  
thereof, in the presence of a catalyst (claim 10),  
and (2) subsequent reaction with m acid halides of formula (III)  
wherein R2, Y and m have the meaning cited above; which process is carried out without  
isolation of the intermediates.

A process (claim 3) according to either claim 1 or claim 2, wherein  
R1 is C1-C12-alkyl, cyclohexyl, phenyl or biphenyl, the radicals phenyl and biphenyl being  
unsubstituted or substituted by one to four C1-C8-alkyl and/or C1-C8-alkoxy;  
R3 is C1-C12-alkyl, cyclohexyl, phenyl or biphenyl, the radicals phenyl and biphenyl being  
unsubstituted or substituted by one to four C1-C8-alkyl and/or C1-C8alkoxy;

A process (claim 4) according to either claim 1 or claim 2, wherein  
R2 is phenyl which is substituted in 2,6- or 2,4,6-position by C1-C4alkyl and/or C-C4-  
alkoxy.

A process (claim 6) according to either claim 1 or claim 2, wherein Y in formula (II) is  
chloro.

A process (claim 7) according to either claim 1 or claim 2, wherein the reaction (I) is carried  
out using lithium, **sodium** or potassium.

A process (claim 8) according to claim 7, wherein from 4 to 6 atom equivalents of the alkali  
metal are used for the preparation of compounds of formula 1, wherein m is 2, and 2 to 3  
atom equivalents of the alkali metal are used for the preparation of compounds of formula  
1, wherein m is 1.

A process (claim 9) according to either claim 1 or claim 2, wherein Y in the compounds of  
formula III is chloro.

A process (claim 11) according to either claim 1 or claim 2, which comprises carrying out

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the reaction (1) of the organic phosphorus halides (II) with an alkali metal in the temperature range from -20 to +120°C

A process (claim 13) according to either claim 1 or claim 2, wherein the reaction (2) of the metallised phosphine with the acid chloride (III) is carried out at -20 to +80°C.

A process (claim 14) according to either claim 1 or claim 2, wherein the reaction steps (1) and (2) are carried out in the same solvent, preferably in tetrahydrofuran.

The catalyst according to D1 (see page 8, paragraph 4) may be an aromatic hydrocarbon having heteroatoms. within this definition falls the activator chlorobenzene according to claim 4.

The subject-matter of claims 1-4 and 6-9, therefore, differs from this known D1 process only in that the alkali metal selected is sodium and is present in the form of a dispersion of alkali metal particles having a mean size of  $\geq 500 \mu\text{m}$  in the solvent.

The process claim 5 additionally differs from this known D1 process in the use of a high speed stirrer. The features according to claims 5 and 6 belong to the common knowledge of the skilled person and can thus not be a reason for an inventive merit (high speed agitation, see D4, column 2, line 36; D2, column 2, line 13).

The problem to be solved by the present invention may therefore be regarded as making available a new process for preparing compounds of formula (I).

The solution proposed in claims 1-9 of the present application cannot be considered as involving an inventive step (Article 33(3) PCT) for the following reasons:

Sodium metal when used as a reagent is in the form of a dispersion of the metal in the solvent. The particle size is usually less than  $500 \mu\text{m}$  in commercially available material as can be seen from the epodoc logfile printouts 32/32 of WO8706234 and 19/32 (US4987202). Other hits 3/32 and 7/32 -9/32 just like D5 show that a particle size of less than  $500 \mu\text{m}$  is connected to the feature "sodium dispersion".

All the documents show that the selected particle size in claim 1 is virtually no limiting factor. No document has been found during the search in which the particle size of an



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(SEPARATE SHEET)**

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alkali metal in the dispersion is above the limit of present claim 1. Hence, the skilled person knows that a sodium dispersion in which the particle size is less than 500  $\mu\text{m}$  is normally employed in chemical reactions.

Claims 1-9, therefore, lack inventive merit over the combination of D1 and the knowledge of the skilled person.

Printed: 16/06/2005

CLMSPAMD

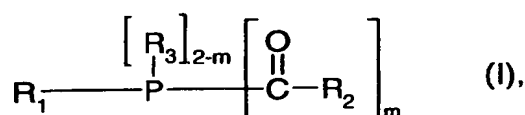
EP 04763601

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## Claims

1. A process for the preparation of acylphosphines of formula (I)

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wherein

m is 1 or 2;

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$R_1$  is  $C_1$ - $C_{18}$  alkyl,  $C_2$ - $C_{18}$  alkyl which is interrupted by one or several non-successive O atoms, phenyl substituted  $C_1$ - $C_4$  alkyl,  $C_2$ - $C_8$  alkenyl, phenyl, naphthyl, biphenyl,  $C_5$ - $C_{12}$  cycloalkyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl,  $C_5$ - $C_{12}$  cycloalkyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen,  $C_1$ - $C_8$  alkyl,  $C_1$ - $C_8$  alkylthio and/or  $C_1$ - $C_8$  alkoxy;

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$R_2$  is  $C_1$ - $C_{18}$  alkyl,  $C_3$ - $C_{12}$  cycloalkyl,  $C_2$ - $C_{18}$  alkenyl, phenyl, naphthyl, biphenyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl or 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to four  $C_1$ - $C_8$  alkyl,  $C_1$ - $C_8$  alkoxy,  $C_1$ - $C_8$  alkylthio and/or halogen;

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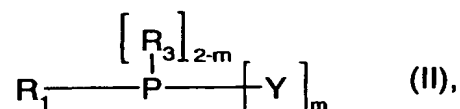
$R_3$  is  $C_1$ - $C_{18}$  alkyl,  $C_2$ - $C_{18}$  alkyl which is interrupted by one or several non-successive O atoms; phenyl substituted  $C_1$ - $C_4$  alkyl,  $C_2$ - $C_8$  alkenyl, phenyl, naphthyl, biphenyl,  $C_5$ - $C_{12}$ -cycloalkyl or a 5- or 6-membered O-, S- or N-containing heterocyclic ring, the radicals phenyl, naphthyl, biphenyl,  $C_5$ - $C_{12}$  cycloalkyl or the 5- or 6-membered O-, S- or N-containing heterocyclic ring being unsubstituted or substituted by one to five halogen,  $C_1$ - $C_{18}$  alkyl,  $C_1$ - $C_8$  alkylthio and/or  $C_1$ - $C_8$  alkoxy;

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by

## 13

(1) reacting organic phosphorus halides of formula (II)



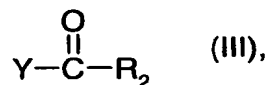
5

wherein  $R_1$ ,  $R_3$  and  $m$  have the meaning cited above;  
and  $Y$  is Br or Cl,

with sodium in a solvent in the presence of an activator, wherein sodium is present in the form of a dispersion of sodium particles having a mean particle size of  $\leq 500 \mu m$  in the solvent,

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(2) subsequent reaction with acid halides of formula (III)



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wherein  $R_2$  and  $Y$  have the meaning cited above;  
which process is carried out without isolation of the intermediates.

2. The process according to claim 1, wherein  $R_1$ ,  $R_2$  and  $R_3$  are independently from each other phenyl, naphthyl and biphenyl, being unsubstituted or substituted by one to five halogen,  $C_1$ - $C_8$  alkyl and/or  $C_1$ - $C_8$  alkoxy.

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3. The process according to claim 2, wherein  $R_1$  and  $R_3$  are phenyl and  $R_2$  is 2,4,6-trimethylphenyl.

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4. The process according to any one of claims 1 to 3, wherein the activator is chlorobenzene and/or n-butanol.

5. The process according to any one of claims 1 to 4, wherein the alkali metal is dispersed in the solvent by means of a high speed turbine stirrer.

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6. A process according to any one of claims 1 to 5, wherein from 4 to 8 atom equivalents of the alkali metal are used for the preparation of compounds of formula (I), wherein  $m$  is 2, and 2 to 4 atom equivalents of the alkali metal are used for the preparation of compounds of formula (I), wherein  $m$  is 1.

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7. A process according to any one of claims 1 to 6, wherein the reaction (1) of the organic phosphorus halides (II) with an alkali metal is carried out in the temperature range from  $-20^{\circ}$  to  $+160^{\circ}\text{C}$ .

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8. A process according to any one of claims 1 to 7, wherein the reaction (2) of the metallised phosphine with the acid chloride (III) is carried out at  $-20^{\circ}$  to  $+120^{\circ}\text{C}$ .

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9. A process according to any one of claims 1 to 8, wherein the reaction steps (1) and (2) are carried out in toluene or ethyl benzene as solvent.